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(54) Title: ANODES FOR ELECTROPLATING OPERATIONS, AND METHODS OF FORMING MATERIALS OVER SEMI-
CONDUCTOR SUBSTRATES

(57) Abstract: The invention includes anodes for electroplating baths. The anodes have a purity of at least 99.9%, and comprise one
or more of silver, gold, nickel, chromium, copper or various solder compositions. The anodes can, for example, comprise at least
99.995% copper/phosphorus alloy, by weight; or at least 99.995% nickel and sulfur, by weight. The invention also includes methods
of electroplating materials over semiconductor substrates.

Anodes for Electroplating Operations, and Methods of Forming Materials Over Semiconductor Substrates

TECHNICAL FIELD

[0001] The invention pertains to methodology for electroplating materials over semiconductor substrates. In particular aspects, the invention pertains to anodes for utilization in electroplating operations. In other aspects, the invention pertains to metals having a purity of at least 99.995%, and suitable for utilization in charging the electrolyte of an electrolytic bath.

BACKGROUND OF THE INVENTION

[0002] Electroplating methods are utilized for numerous applications in which it is desired to form a metal-containing layer over a substrate. An exemplary prior art electroplating apparatus 10 is described with reference to Fig. 1. Apparatus 10 comprise a vessel 12 which retains a liquid 14 (specifically, an electrolyte solution) therein. Vessel 12 can comprise any suitable material, including, for example, a metal having a non-corrosive liner (not shown) extending along an interior surface of the vessel to protect the metal from reacting with liquid 14. Alternatively, vessel 12 can comprise a plastic or a glass. In some applications, vessel 12 will be configured to enable temperature control of the liquid 14 so that liquid 14 can be maintained at a desired operating temperature during an electroplating process.

[0003] An anode 16 and a substrate 18 are provided within vessel 12. Anode 16 comprises a metal which is ultimately to be plated along a conductive surface of substrate 18. In the shown application, substrate 18 has a conductive surface 20. A power source 22 is provided in electrical connection with anode 16 and substrate 18, and generates a voltage differential between the anode and the substrate. The voltage differential causes conductive material to migrate from anode 16, through electrolytic solution 14, and to conductive surface 20. The conductive material forms a layer 24 of plated conductive material across the surface 20 of substrate 18.

[0004] The transfer of conductive material from anode 16 to substrate 18 is actually a series of mass transfer events. Specifically, conductive material is transferred from anode 16 into electrolyte 14 in a first mass transfer, and subsequently passes from electrolyte 14 to substrate 18 in a second mass transfer. If a starting concentration of the conductive material of anode 16 within electrolyte 14 is low, a significant amount of material from anode 16 can be transferred into electrolyte 14 to establish an equilibrium between electrolyte 14 and anode 16 prior to effective transfer of the anode material to

substrate 18. Such can effectively cause waste of a significant portion of anode 16, in that such portion is utilized to establish an equilibrium rather than being passed to substrate 18. A method of avoiding such waste is to pre-charge electrolyte 14 with conductive material of the type that will be transferred from anode 16. The pre-charging causes electrolyte 14 to start with a concentration of the conductive material that is close to the equilibrium concentration that will be established during an electroplating operation. The precharging can occur by providing particulates of the conductive material of anode 16 within a suitable solvent (such as, for example, an appropriate acid) to dissolve the particulates and form a solution comprising the conductive material of anode 16. The solution can subsequently be added to liquid 14 to form the pre-charged electrolyte 14.

[0005] Electrolyte 14 can comprise any suitable conductive solution. In particular applications, substrate 18 will comprise a semiconductive wafer, such as, for example, a monocrystalline silicon wafer. In such applications, it can be desired to avoid utilization of sodium or potassium in electrolyte 14, as such can influence a conductivity of the semiconductive material. In such applications, suitable salts for inclusion in electrolyte 14 are, for example, copper sulfate for copper baths, nickel sulfamate for nickel baths and fluoroborate for lead/tin baths.

[0006] Another aspect of the prior art pertains to semiconductor processing applications. A fragment of a semiconductor wafer construction 50 is described with reference to Fig. 2. Construction 50 comprises a semiconductor substrate 52. To aid in interpretation of the claims that follow, the terms "semiconductive substrate" and "semiconductor substrate" are defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above.

[0007] Substrate 52 can comprise, for example, a monocrystalline silicon wafer having various insulative and conductive materials formed thereover. Additionally, substrate 52 can comprise numerous circuit components (not shown), which are together incorporated into an integrated circuit.

[0008] A conductive material 54 is formed over substrate 52, and can constitute a wiring layer in electrical connection with circuitry (not shown) associated with substrate 52. Conductive material 54 can comprise, for example, aluminum and/or copper.

[0009] An insulative material 56 is formed over conductive material 54. Insulative material 56 is patterned to have an opening 58 extending therethrough. Conductive

materials 60 and 62 are formed within the opening. Conductive material 60 can comprise, for example, one or more of chromium, cobalt, nickel, copper, silver and gold; and layer 62 can also comprise, for example, one or more of chromium, nickel, copper, silver and gold. In particular applications, layer 60 will comprise nickel and layer 62 will comprise gold.

[0010] A solder bump 64 is formed over layer 62. Solder bump 64 can comprise, for example, a tin-based solder or a lead-based solder, with the term "based" being understood to denote a majority element of solder. Solder bump 64 can ultimately be utilized for forming an electrical connection to circuitry external of substrate 52, and accordingly can be utilized together with layers 54, 60 and 62 to form an interconnect between circuitry (not shown) associated with substrate 52 and other circuitry (not shown) external of substrate 52.

[0011] Materials 54, 60, 62 and 64 can be formed by numerous methods, including, for example, electroplating. Difficulties occur, however, in forming materials 54, 60, 62 and 64 to have desired purity and physical characteristics when utilizing electroplating methods. It would therefore be desirable to develop new methods for electroplating materials over semiconductor substrates.

SUMMARY OF THE INVENTION

[0012] The invention includes anodes for electroplating baths. In particular aspects, the anodes have a purity of at least 99.99%, and comprise one or more of silver, gold, nickel, chromium, cobalt, copper or various solder compositions. The anodes can, for example, comprise at least 99.995% copper/phosphorus alloy, by weight; or at least 99.995% nickel and sulfur, by weight. As another example, the anodes can comprise at least 99.9995% copper, by weight; or at least 99.999% of a solder composition, by weight.

[0013] The invention also encompasses methods of electroplating materials over semiconductor substrates.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

[0015] Fig. 1 is a diagrammatic, cross-sectional view of a prior art electroplating apparatus.

[0016] Fig. 2 is a diagrammatic, cross-sectional, fragmentary view of a prior art semiconductor wafer fragment.

[0017] Fig. 3 is a diagrammatic, isometric view of a billet at a preliminary processing step of a method of the present invention for forming an anode.

[0018] Fig. 4 is a view of a blank formed from the Fig. 3 billet.

[0019] Fig. 5 is an isometric view of another blank which can be utilized in accordance with methodology of the present invention for forming an anode.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0020] Among the problems with prior art anodes (such as the anode 16 described with reference to Fig. 1) are that compositional and physical properties of the anode materials are not tightly controlled during formation of the anodes. The present invention encompasses anode materials having improved compositional and physical properties relative to prior art anode materials.

[0021] Among the compositional parameters that can be controlled by methodology of the present invention are purity and homogeneity. Specifically, methodology of the present invention can enable an anode to be formed from one or more of silver, gold, nickel, chromium, cobalt and copper to a purity of at least 99.99% by weight (i.e., 4N purity, with the term "4N" understood to mean four nines), and in particular aspects to a purity of at least 99.995% (4N5), 99.999% (5N), 99.9999% (6N), or at least 99.99999% (7N).

[0022] Preferably, the anodes will comprise little to no alpha-particle emitting materials, since alpha particles can be severely detrimental to semiconductor constructions. Accordingly, a preferred composition will have less than 3 ppb of uranium and less than 3 ppb of thorium; and preferably will have less than 3 ppb total of uranium and thorium; more preferably less than 1 ppb total of uranium and thorium, and yet more preferably less than 0.5 ppb total of uranium and thorium.

[0023] In further aspects, an anode material of the present invention can comprise at least 99.995%, by weight, (4N5) of copper/phosphorus alloy, with the phosphorus concentration preferably being from about 200 ppm to about 1000 ppm, by weight; such as, for example, from about 200 ppm to about 600 ppm, by weight. The copper/phosphorus alloy can have a purity of 5N, 6N, and even at least 7N. The copper/phosphorus alloy can alternatively be referred to as phosphorus-doped copper. The incorporation of phosphorus can aid in the development of a black oxide film on the anode surface. This film can serve two important functions. First, it can act as a filter by entrapping impurities in the film. Second, the film can regulate the copper dissolution rate, and thus maintain the copper in solution at a consistent and desired level. Also, addition of phosphorus, and/or other alloy elements, can promote grain refinement.

[0024] In another aspect, the anode can comprise at least 99.995% (4N5) nickel and sulfur, by weight; and in particular aspects can comprise 5N, 6N, or at least 7N purity of the nickel/sulfur combination. The sulfur can be present to a concentration of from about 0.01% to about 5%, by weight; and it can be preferred that the sulfur is present to a concentration of from about 0.01% to about 0.04%, by weight. The inclusion of sulfur can be advantageous in that the sulfur can promote grain refinement. Additionally, the sulfur can promote more uniform dissolution of the anode than would occur in the absence of the sulfur. Additionally, addition of sulfur can lower electrical resistance, which can enable lower power consumption during a plating operation. Also, if layer 54 of the Fig. 2 construction 50 comprises copper and layer 60 comprises nickel, it can be advantageous to have sulfur incorporated within material 60 during electrolytic deposition of the material 60 to improve adhesion of nickel-containing material 60 to copper-containing layer 54.

[0025] In other aspects of the invention, a composition of an anode can correspond to a high-purity solder composition, such as, for example, a solder composition having a purity of at least 99.99% by weight (4N), with such composition including one or more elements selected from the group consisting of tin, antimony, lead, silver, copper and bismuth. In further aspects, the solder composition can have a purity of at least 5N, 5N5, 6N, 6N5 or 7N. Exemplary solder compositions comprise at least 5N purity of tin; tin/antimony; tin/lead; tin/silver; tin/silver/copper; silver/bismuth; and tin/copper.

[0026] Phosphorus can be included in solder alloys. If phosphorus is included, it will preferably be provided to a concentration of less than 1,000 ppm, such as, for example, a concentration of from greater than 0 ppm to 500 ppm.

[0027] It can be preferred that the solder be lead-free in order to reduce the amount of alpha-particle emitting materials in the composition. Specifically, there are naturally occurring isotopes of lead whose decay chain results in the emission of an alpha particle. Furthermore, these lead isotopes cannot be removed from the lead using conventional refining means. Suitable lead-free compositions are tin/silver, tin/bismuth, tin/silver/copper, bismuth/silver and tin/copper. The concentration of uranium in such compositions is preferably less than 3 ppb, and the composition of thorium is preferably also less than 3 ppb. In particular aspects, a combined total of uranium and thorium is less than 3 ppb in a solder-composition anode of the present invention. Further, a preferred anode comprising a solder composition of the present invention will preferably have an alpha count of less than or equal to 0.001 counts/(cm²·hr), more preferably less than 0.02 counts/(cm²·hr), and even more preferably less than 0.002 counts/(cm²·hr). An advantage of eliminating alpha-particle emitters from solder is that alpha particles can adversely impact performance, primarily in the area known as soft errors. As line

widths decrease, it is possible for alpha particles to permanently damage circuitry. Another advantage is that the elimination or reduction of lead can lead to a cleaner waste stream from an electrolytic deposition process.

[0028] An exemplary method of forming an anode composition comprising at least 5N pure copper, silver and gold is vacuum casting.

[0029] Exemplary methods of forming an anode composition comprising at least 4N purity of one or more of nickel and chromium include hot pressing and vacuum casting.

[0030] An exemplary method of forming a composition comprising copper/phosphorus, having a purity of at least 5N, and a phosphorus concentration of about 200 ppm to about 1000 ppm utilizes vacuum casting and a master alloy. The purification of copper can be accomplished by electrorefining.

[0031] An exemplary method of forming a nickel composition comprising at least 4N5 purity of nickel and sulfur, with a sulfur concentration of about 0.01% to about 5%, by weight, utilizes vacuum casting and a master alloy. Another exemplary method is to combine nickel and sulfur powders, and to then hot press the combination to a near net shape corresponding approximately to a desired final shape.

[0032] An exemplary method of forming an anode composition comprising at least 5N purity of one or more of tin, antimony, lead, silver, copper and bismuth; and suitable for electrolytic deposition of a solder bump, comprises casting an alloy of the desired materials.

[0033] Another compositional aspect of the various anode materials of the present invention is the homogeneity of such materials. The term "homogeneity" is utilized in reference to the materials to indicate that the anode materials preferably have a uniform composition throughout an entirety of an anode, and that inclusions and precipitates are finely dispersed. Preferably, inclusions and precipitates will be no more than 10 micrometers in average size. In particular applications, an average length of all inclusions and precipitates along a maximum dimension of the individual inclusions and precipitates will be less than or equal to 10 micrometers, more preferably less than 1 micrometer, and; yet more preferably an average length of all inclusions and precipitates will be less than or equal to one-tenth micrometer.

[0034] Among the physical characteristics that can be controlled within an anode composition utilizing methodology of the present invention are texture and grain size. Specifically, an average grain size throughout an anode of the present invention will preferably be less than 100 micrometers, more preferably less than 50 micrometers, even more preferably less than 10 micrometers, and in particular embodiments less than 1 micrometer. The average grain size can be determined by standard methods of the art. In particular aspects of the invention, an average of the maximum dimensions of

the grains of an anode will be less than 100 micrometers, more preferably less than 50 micrometers, even more preferably less than 10 micrometers, and in particular embodiments less than 1 micrometer. For purposes of the interpreting this disclosure and the claims that follow, an anode referred to as having a stated average grain size is to be understood as having such average grain throughout all of the grains of the anode unless it is specifically stated that only a portion of the anode has the stated average grain size.

[0035] The above-described preferred grain sizes can be relevant to any of the anode compositions encompassed by the present invention, including, for example, the compositions consisting essentially of, or consisting of, one or more of copper, nickel, silver, gold, chromium, cobalt, tin, antimony, lead and bismuth.

[0036] The term "texture" refers to the distribution of crystallographic orientations, with a material having a relatively random distribution of orientations being referred to as having a weak texture, and a material having a relatively non-random distribution being referred to as having a strong texture. Anodes of the present invention can be microstructurally textured so that the different grains of metal erode at the same rate. It is well known that different crystallographic planes will erode at different rates in most electrolytic cells, and advantage is taken of this fact to etch metallographic samples so that the different grains are visible during visual microscopic examination. In embodiments in which the anode microstructure is textured so that the grains all expose the same crystallographic face (or faces that are very close to being the same), differential erosion of the anode can be reduced, minimized, or even eliminated. Such can lead to relatively uniform erosion of an anode. The uniform erosion can lead to a more uniform plated film than would otherwise occur, as well as a longer anode lifetime, and less particulate in the plating bath. Accordingly, utilization of an appropriate texture in anodes of the present invention can improve the uniformity of dissolution of the anodes into a plating bath, which can ultimately both extend the life of the anode and improve a uniformity of an electroplated film formed from the anode. A uniform, and substantially random texture can be desired for various anodes, including an anode consisting essentially of copper, copper/phosphorus, nickel, nickel alloy or nickel/sulfur; consisting essentially of chromium or chromium alloy; consisting essentially of silver or silver alloy; or consisting essentially of a solder composition comprising one or more elements selected from the group consisting of tin, antimony, lead, silver, copper and bismuth.

[0037] In one aspect, an advantage of texture control in an anode can be described by considering each grain within a metal object as a crystal with its crystal lattice oriented in some particular way relative to a reference plane. The reference plane can

be, for example, the erosion surface of the anode. Since each grain is independent of the others, each grain lattice has its own orientation relative to this plane. When grain orientation is not random, but crystal planes tend to be aligned in some way relative to a reference plane, the material is said to have a non-random "texture". These textures are denoted using standard indices, which define directions relative to crystallographic planes. For instance, an anode made from a metal with cubic crystal structure, such as copper, may have a $\langle 100 \rangle$, a $\langle 110 \rangle$ or other textures. Similarly, an anode made from a metal with hexagonal crystal structure, such as cobalt, may have a $\langle 0002 \rangle$ texture. The exact texture developed will depend on the metal type and the work and heat treatment history of the anode. Miller indices, denoted by the numeric indices enclosed in "()", are also used to describe families of planes or orientations in symmetric crystal structures. Different textures can be produced in most metals by altering their thermomechanical processing.

[0038] The effect of crystallographic orientation of a sputtering target on sputtering deposition rate and film uniformity has been described in an article by C. E. Wickersham, Jr., entitled Crystallographic Target Effects in Magnetron Sputtering in the J.Vac. Sci. Technol. A5(4), July/August 1987 publication of the American Vacuum Society. In this article, the author indicates that improvements in film uniformity may be achieved on a silicon wafer by controlling the working process for making a target. Several US patents have issued which teach how to control the texture of a sputtering target for optimal performance in many applications (see, for example, US patents 6302977, 6238494, 5993621, 5809393, 5780755, 5087297). The patents do not, however, indicate that the control of texture would have any application relative to the formation of anodes for use in electroplating baths.

[0039] Crystallographic structure can influence the corrosion or dissolution behavior of a material, as demonstrated by etching a material for metallographic evaluation. Differently oriented grains will "etch" or be eroded to different degrees. Therefore, controlling the texture or uniformity of grain orientation of an anode can be advantageous to uniform dissolution and hence uniform film deposition. Control of the texture can be done in two exemplary forms – control of dominant texture orientation, and control of texture intensity.

[0040] The intensity of the texture, or relative fraction of grains that share a common orientation, can be important for uniform dissolution. If a random texture (low intensity for any specific texture and a random orientation of grains) is present, then those grains that are oriented favorably will erode faster, creating a non-uniform surface. There can be a weak texture present, where one orientation is preferred or more common than others, but a significant fraction of the grains exhibit an orientation different from this.

Very strong textures, in which a high percentage of grains have the same orientation, can therefore result in more uniform erosion.

[0041] Specific desired textures for particular anodes can depend upon the material and geometric features of the anode. For example, for a flat surface, a texture which aligns the close packed planes with the anode surface, may be advantageous. For cobalt, an HCP metal, this would be the (001) planes, or a (001) texture. For FCC metals such as copper, this would be a (111) texture, while for BCC metals such as chromium, this would be a (110) texture. In particular aspects, the invention includes anodes having at least 25% of the grains, at least 50% of the grains, at least 75% of the grains, or at least 90% of the total number of grains with a specific desired crystallographic texture. For HCP metals the specific desired texture will typically be (001), for FCC metals the specific desired texture will typically be (111), and for BCC metals the specific desired texture will typically be (110).

[0042] Exemplary methods for forming desired grain sizes and textures within anode compositions of the present invention are described with reference to Figs. 3-5.

[0043] Referring to Fig. 3, a billet 100 of an anode composition is illustrated. Billet 100 can be formed by melting one of the above-described anode compositions, pouring the composition into a mold, and cooling the composition into a cylindrical shape. In other words, the anode material can be cast into a cylindrical shape. The cylindrical shape can be used directly as billet 100. Alternatively, one or both of the ends of the cast cylindrical shape can be cut to remove cavities or other defects that may be associated with the ends prior to utilization of the cast material as billet 100. Billet 100 has a width 105 and a length 110.

[0044] The material of the billet may be utilized in the as-cast form. Alternatively, the material of billet 100 can be thermomechanically processed into the desired shape of the billet while imparting a desired grain size and texture to the material. Also, a gradient freeze can be utilized during a casting process. The gradient freeze can form a columnar microstructure within the material of billet 100. Yet another method of forming billet 100 is to subject the material of billet 100 to a long term thermal treatment (such as a long term heating treatment) to form billet 100 as a single crystal.

[0045] Referring to Fig. 4, a blank 101 is illustrated. Blank 101 can be formed by subjecting billet 100 (Fig. 3) to various thermomechanical processes, such as, for example, hot-forging, rolling and/or cross-rolling. The thermomechanical processing has increased the width of the billet to a new width 115, and decreased the length to a new length 120. A ratio of change in length 120 to length 110, divided by length 110, corresponds to a reduction ratio of blank 101 relative to billet 100. Preferably such reduction ratio will be from about 50% up to 90%. The thermomechanical processing

can reduce an average grain size of the anode material, reduce particulate sizes, reduce inclusion sizes, and disperse inclusions throughout the anode material. Additionally, the thermomechanical processing can induce a desired texture. The texture, grain size, particulate size and inclusion size can be further influenced by subjecting the blank of Fig. 4 to thermal processing, in addition to the mechanical processing techniques of forging, rolling and cross-rolling.

[0046] If blank 101 is subjected to sufficient thermomechanical processing, an average grain size within the blank can be reduced to less than 100 microns. Additionally, a texture within the blank can be transformed into a random texture; or in particular applications to a strong texture oriented in a desired direction. Suitable thermomechanical processes are described in U.S. Patent Numbers 6,238,494; 6,113,761; 5,993,621; and 5,780,755, which are incorporated herein by reference.

[0047] Fig. 5 illustrates another blank which can be utilized in methodology of the present invention. Specifically, Fig. 5 illustrates a blank 150 having a substantially square shape. Blank 150 can be cut from the blank of Fig. 4, for example. Blank 150 can be subjected to equal channel angular extrusion (ECAE) to randomize the texture within the blank, and to reduce average grain size to less than 100 microns, less than 50 microns, less than 10 microns, and in particular applications to less than 1 micron. ECAE methodology is described in, for example, U.S. Patent Numbers 5,600,989 and 5,780,755, which are hereby incorporated by reference. Grain size reduction and texture randomization can be accomplished by utilizing a sufficient number of passes (preferably at least four, and frequently at least six) through an ECAE apparatus, while rotating the blank 150 between passes so that the blank has different orientations from one pass to another.

[0048] The materials produced by the processing described with reference to Figs. 3-5 can be utilized as anodes in electrolytic apparatuses, such as, for example, the prior art apparatus described with reference to Fig. 1. Further, such materials can be cut, pressed or rolled to produce powders, pellets, rolled strips or other forms that can be readily dissolved in a suitable acid to form a pre-charged electrolyte. The pellets and powders can be referred to as particulate forms of the material. The powder, pellets or rolled strips can be referred to as metallic materials. Any suitable acid can be utilized for dissolving the particulates and/or metallic materials. An exemplary acid for dissolving the metallic materials corresponding to solder-composition-containing anodes is methyl-sulfonic acid, and an exemplary acid for dissolving copper-composition-containing anodes is sulfuric acid.

[0049] An anode material of the present invention can be incorporated into an electrolytic deposition process for forming one or more of the conductive layers shown in

the semiconductor construction 50 of Fig. 2. Specifically, the invention encompasses a process wherein a semiconductor substrate is provided and a wiring layer (such as the wiring layer 54 of Fig. 2) is formed over the substrate. Such wiring layer can be formed by sputter-deposition of a copper-seed layer, and subsequent electrolytic deposition of copper over the seed layer. The copper can be deposited from an anode formed in accordance with the present invention, and accordingly having a purity of at least 4N5, and a reduced number of inclusions and particulates. It can be desired to avoid having inclusions and particulates in an anode, as the inclusions and particulates can behave differently than surrounding anode material during electrolytic deposition, and can thus cause inhomogeneities in electrochemically deposited materials. In particular embodiments, at least some of wiring layer 54 is electrolytically deposited from an anode consisting essentially of copper, or copper and phosphorus.

[0050] After formation of wiring layer 54, the mask 56 is formed, and subsequently under-bump material 60 is electrochemically deposited on wiring layer 54. Material 60 can comprise at least one of silver, nickel, chromium, cobalt and copper, and can be electrochemically deposited from an anode that is at least 99.995% pure in silver, from an anode that is at least 99.995% pure in nickel, or from an anode that is at least 99.995% pure in one or more of nickel, chromium, cobalt, copper and silver.

[0051] Numerous metals can be incorporated into under-bump metallurgy utilizing methodology of the present invention. For instance, chromium is often used as part of the under-bump metallurgy between the circuit pad on the silicon die and the solder that compromises the flip chip bumps. The chromium adheres strongly to the circuit pad metal (often Al) and forms a diffusion barrier between the remainder of the under-bump metallurgy and the circuitry. The chromium utilized is typically a series of Cr/Cu layers, and such are generally created by evaporation in prior art methods. However, Cr and Cu can be plated in accordance with methodology of the present invention to create the Cr/Cu layers.

[0052] After formation of under-bump layer 60, the second under-bump layer 62 can be formed on layer 60. In particular embodiments, layer 60 will consist essentially of nickel, or consist essentially of nickel and sulfur, and layer 62 will consist essentially of silver. Layer 62 can accordingly be deposited from an anode that is at least 4N5 pure in silver. Alternatively, layer 62 can comprise, consist essentially, of or consist of other metals in addition to, or alternatively to, silver. For instance, layer 62 can be deposited from an anode that is at least 4N5 pure in one or more of silver, chromium and copper.

[0053] Solder layer 64 is subsequently formed over layer 62. Layer 64 can be formed from an anode that is at least 4N pure in one or more elements selected from the group consisting of tin, antimony, lead, silver, copper and bismuth.

[0054] The construction 50 formed in accordance with methodology of the present invention can be utilized in, for example, flip-chip technologies or wafer scale packaging.

[0055] The processes described above are exemplary processes, and it is to be understood that the invention encompasses other embodiments in addition to those specifically described. For instance, the invention encompasses an embodiment in which an anode material is utilized for electrolytic deposition of a main interconnect circuit. Specifically, the invention encompasses a process wherein a semiconductor substrate is provided with trenches and or vias etched therein. A continuous barrier layer is then deposited by a PVD or CVD process. A conductive metal seed layer, preferably Cu or Cu alloy, is then deposited by PVD, CVD, or electroless deposition. The bulk of a semiconductor feature is then formed via electrochemical deposition of copper. The copper can be deposited from an anode formed in accordance with the present invention, and accordingly have a purity of at least 4N5, and having a reduced number inclusions and particulates.

[0056] Among the advantages of utilizing highly pure anode and pre-charge materials of the present invention relative to prior art materials, is that the materials of the present invention can improve bath time life of an electrolytic bath; can improve anode life; can improve deposited film composition, quality and uniformity;; and can thus reduce costs associated with electrolytic deposition methodologies.

[0057] The invention has been described with reference to several exemplary processes. It is to be understood, however, that the invention encompasses embodiments having numerous modifications and variations relative to the above-described exemplary processes. Several exemplary modifications and variations are described next.

[0058] In one variation, a surface coating can be applied to portions of the anode so that these portions are not eroded by the electrolyte during plating. One method of applying such coating is to flame spray the coating on a portion of the anode that is to be protected. Flame spraying can enable a material which is brittle and/or which has a much higher melting point than the anode composition to be applied to an anode. The applied material can then serve as a protective barrier. For example, a relatively inert metal (such as, for example, Ti) or a ceramic (such as, for example, alumina) could be flame sprayed on a Cu-comprising anode. In other exemplary applications, other materials can be flame sprayed on a wide range of anodes to produce a non-erodible surface layer. Alternatively, another method of applying a protective coating is to powder coat with a polyethylene coating.

[0059] In another variation, a compensation can be patterned into an anode to compensate for an erosion profile. As anode dissolution progresses over the useful

lifetime of the anode, the surface of the anode develops an erosion profile. The erosion profile is based on a number of characteristics specific to anode, and to the set-up and operation of the plating equipment. These include, but are not limited to, the anode material, cell geometry, anode to cathode ratio, plating chemistry, current density, shielding, and fluid dynamics within the cell. Two factors will determine the useful lifetime of an anode. As the erosion profile becomes more pronounced, it will affect the uniformity of the thin film being deposited across the wafer surface. The amount of non-uniformity that a specific user can tolerate will limit anode life. The second factor is burn-through of a the anode, in which the erosion actually perforates the bottom side of the anode. An absence of material in the surface of the anode can drastically impact thin film uniformity. Once the erosion profile has been identified for a specific process, a compensatory design can be developed which will add material to the anode surface in direct relationship to the rate in which those areas erode. This can have the beneficial effect of extending anode life with acceptable deposition characteristics versus just adding overall thickness, which would only amplify the erosion profile at the end of the life cycle.

[0060] In another variation, "special" packaging of an anode can be designed for shipping and handling of anodes. The special packaging can reduce or eliminate the handling of the anodes during installation of the anode into a plating reactor, which can reduce introduction of impurities into a plating bath. The special packaging can also reduce exposure of anodes to oxygen during shipping to eliminate or reduce oxidation of high purity anode materials during the shipping. For example, vacuum packaging of anodes may be useful to reduce the amount of oxygen that a high purity anode is exposed to during shipment, which can reduce oxidation of the anode.

[0061] In another variation, a roughened texture can be imparted to one or more surfaces of an anode. Doing so can increase the surface area of a given part, which can improve the dissolution rate of material from the anode. This may be particularly advantageous during the initial or burn-in period of an anode, where it is desired to quickly come to equilibrium in the bath. There are many methods for imparting a roughened surface to an object. Some textures, such as knurling, may be produced by machining the object. Other rough surfaces may be produced by bead blasting a surface, or impinging a surface with an abrasive media. Chemical etching is another way of roughening a surface.

[0062] Bead blasting is generally very economical, but can have a disadvantage of embedding pieces of the bead media into an anode surface. This can be particularly problematic for soft materials, such as solder anodes. One improved method of bead blasting is to use dry ice as the blast media. The dry ice will sublime and hence leave

no residue on the anode. The anode will generally be suitable for use after bead blasting with dry ice, and a cleaning associated with utilization of either bead-blasting with conventional bead media, or machining (in which case oils are typically required to be cleaned from a surface of the machined part), can be avoided.

[0063] In another variation, anodes can be cast so that they are composed of one or a small number of grains that have a preferred crystallographic texture. Such casting can eliminate high energy grain boundaries which preferentially erode in an electrolyte solution. The anode can be cast by pouring the metal of the anode composition into a mold that has been heated to a temperature above the melting point of the metal, and then cooling the metal slowly from one side or end of the mold. Slow cooling can lead to nucleation of a small number of grains, which then grow. The cooling is normally done from the bottom side of the mold, which results in a microstructure composed a small number of grains that have approximately parallel sides (such grain microstructure is often referred to as a columnar microstructure). The columnar microstructure can virtually eliminate a cause of particulate formation. Specifically, the columnar microstructure can virtually eliminate a problem in which particulate formation occurs through erosion of the grain boundaries around a small grain, followed by the small grain breaking off and forming a particulate in an electrolyte solution.

[0064] In another variation, anodes can be manufactured utilizing different methods of manufacturing than casting and thermomechanically processing. An exemplary method is to extrude the shape of an anode material to a near net shape of a desired anode, and to then cut the material to a desired thickness. This process can be used for tubular parts, as well as solid parts.

[0065] In another variation, a protective coating can be applied over a portion of the anode is to protect the entry point of the electrode into the anode. This coating can be used to prevent erosion of the anode where the anode and electrode connect. Such corrosion can be particularly problematic as the electrolytic bath is consuming the anode. If no protective coating were applied, electrical contact could degrade as the anode erodes.

CLAIMS

1. An anode for an electroplating bath comprising a total number of grains therein, and wherein at least 25% of the total number of grains have a common crystallographic texture as one another.
2. The anode of claim 1 wherein at least 50% of the total number of grains have the common crystallographic texture as one another.
3. The anode of claim 1 wherein at least 75% of the total number of grains have the common crystallographic texture as one another.
4. The anode of claim 1 wherein at least 90% of the total number of grains have the common crystallographic texture as one another.
5. The anode of claim 1 wherein the common crystallographic texture is (001).
6. The anode of claim 1 wherein the common crystallographic texture is (110).
7. The anode of claim 1 wherein the common crystallographic texture is (111).
8. The anode of claim 1 comprising an HCP metal, and wherein the common crystallographic texture is (001).
9. The anode of claim 1 comprising cobalt, and wherein the common crystallographic texture is (001).
10. The anode of claim 1 comprising a BCC metal, and wherein the common crystallographic texture is (110).
11. The anode of claim 1 comprising chromium, and wherein the common crystallographic texture is (110).
12. The anode of claim 1 comprising an FCC metal, and wherein the common crystallographic texture is (111).
13. The anode of claim 1 comprising copper, and wherein the common crystallographic texture is (111).
14. An anode for an electroplating bath comprising an average grain size of less than 100 micrometers.

15. The anode of claim 14 comprising an average grain size of less than 50 micrometers.
16. The anode of claim 14 comprising an average grain size of less than 10 micrometers.
17. The anode of claim 14 comprising an average grain size of less than 1 micrometer.
18. The anode of claim 14 comprising predominantly one or more of silver, gold, nickel, cobalt and chromium by weight.
19. An anode for an electroplating bath and having an alpha particle emission rate of less than 0.1 counts/(cm² hr).
20. The anode of claim 19 having an alpha particle emission rate of less than 0.02 counts/(cm² hr).
21. The anode of claim 19 having an alpha particle emission rate of less than 0.002 counts/(cm² hr).
22. The anode of claim 19 comprising less than 3 ppb total of thorium and uranium.
23. The anode of claim 19 comprising less than 1 ppb total of thorium and uranium.
24. The anode of claim 19 comprising less than 0.5 ppb total of thorium and uranium.
25. The anode of claim 19 comprising one or more of bismuth, silver, tin, lead, copper, nickel, chromium, and cobalt.
26. An anode for an electroplating bath comprising at least 99.99% of one or more of silver, gold, nickel, chromium and cobalt, by weight.
27. The anode of claim 26 comprising at least 99.99% silver.
28. The anode of claim 26 comprising at least 99.99% gold.
29. The anode of claim 26 comprising at least 99.99% chromium.
30. The anode of claim 26 comprising at least 99.99% cobalt.

31. The anode of claim 26 comprising at least 99.99% nickel.
32. The anode of claim 26 comprising at least 99.9995% of the one or more of silver, gold, nickel, chromium and cobalt.
33. The anode of claim 26 comprising less than 3 parts per billion of uranium, and further comprising less than 3 parts per billion of thorium.
34. The anode of claim 26 comprising an average grain size of less than 100 micrometers.
35. The anode of claim 26 comprising an average grain size of less than 50 micrometers.
36. The anode of claim 26 comprising an average grain size of less than 10 micrometers.
37. The anode of claim 26 comprising an average grain size of less than 1 micrometer.
38. The anode of claim 26 comprising at least 99.995% nickel, by weight.
39. The anode of claim 38 comprising an average grain size of less than 100 micrometers.
40. The anode of claim 38 comprising an average grain size of less than 50 micrometers.
41. The anode of claim 38 comprising an average grain size of less than 10 micrometers.
42. The anode of claim 38 comprising an average grain size of less than 1 micrometer.
43. The anode of claim 38 comprising at least 99.9995% nickel.
44. An anode for an electroplating bath comprising at least 99.999% copper, by weight.
45. The anode of claim 44 comprising at least 99.9995% copper.

46. The anode of claim 44 comprising an average grain size of less than 100 micrometers.
47. The anode of claim 44 comprising an average grain size of less than 50 micrometers.
48. The anode of claim 44 comprising an average grain size of less than 10 micrometers.
49. The anode of claim 44 comprising an average grain size of less than 1 micrometer.
50. The anode of claim 44 comprising less than 3 parts per billion of uranium, and further comprising less than 3 parts per billion of thorium.
51. An anode comprising at least 99.995%, by weight, copper/phosphorous alloy.
52. The anode of claim 51 wherein the phosphorus concentration is from about 200 ppm to about 1000 ppm, by weight.
53. The anode of claim 51 comprising an average grain size of less than 100 micrometers.
54. The anode of claim 51 comprising an average grain size of less than 50 micrometers.
55. The anode of claim 51 comprising an average grain size of less than 10 micrometers.
56. The anode of claim 51 comprising an average grain size of less than 1 micrometer.
57. An anode for an electroplating bath comprising at least 99.995% nickel and sulfur, by weight.
58. The anode of claim 57 comprising from about 0.01% sulfur to about 5% sulfur, by weight.
59. The anode of claim 57 comprising an average grain size of less than 100 micrometers.

60. The anode of claim 57 comprising an average grain size of less than 50 micrometers.
61. The anode of claim 57 comprising an average grain size of less than 10 micrometers.
62. The anode of claim 57 comprising an average grain size of less than 1 micrometer.
63. An anode for an electroplating bath comprising a solder composition having a purity of at least 99.999%, by weight; said solder composition comprising one or more elements selected from the group consisting of tin, antimony, lead, silver, copper and bismuth.
64. The anode of claim 63 comprising an average grain size of less than 30 micrometers.
65. The anode of claim 63 comprising an average grain size of less than 10 micrometers.
66. *The anode of claim 63 comprising an average grain size of less than 5 micrometers.*
67. The anode of claim 63 comprising an average grain size of less than 1 micrometer.
68. The anode of claim 63 comprising at least 99.9995% solder.
69. The anode of claim 63 comprising less than 3 parts per billion of uranium, and further comprising less than 3 parts per billion of thorium.
70. The anode of claim 63 comprising at least 99.999% tin.
71. The anode of claim 63 wherein the solder composition comprises tin and antimony.
72. The anode of claim 63 wherein the solder composition comprises tin and lead.
73. The anode of claim 63 wherein the solder composition comprises tin and silver.
74. The anode of claim 63 wherein the solder composition comprises tin, silver and copper.

75. The anode of claim 63 wherein the solder composition comprises silver and bismuth.
76. The anode of claim 63 wherein the solder composition comprises tin and copper.
77. A method of forming materials over a semiconductor substrate, comprising:
providing a semiconductor substrate having a wiring layer thereon;
electrolytically depositing at least one of silver and nickel over the wiring layer;
any silver being deposited from an anode that is at least 99.995% pure in silver; and any
nickel being deposited from an anode that is either at least 99.995% pure in nickel, or at
least 99.995% pure in nickel and sulfur, with the sulfur being present to a concentration
of from about 0.01% to about 5%, by weight; and
forming a solder over the at least one of silver and nickel.
78. The method of claim 77 wherein the wiring layer comprises copper, and is
formed by electrolytic deposition utilizing an anode that is either at least 99.999%
copper, by weight, or at least 99.995% copper/phosphorous alloy, with the phosphorus
concentration being from about 200 ppm to about 1000 ppm, by weight.
79. The method of claim 77 wherein the solder is formed by electrolytic deposition
utilizing an anode that comprises a solder composition having a purity of at least
99.999%, by weight; said solder composition comprising one or more elements selected
from the group consisting of tin, antimony, lead, silver, copper and bismuth.
80. The method of claim 77 wherein the electrolytic deposition forms nickel over the
wiring layer; the electrolytic deposition occurs in a bath, and the bath is initially charged
with metallic materials that are either at least 99.995% pure in nickel, or at least
99.995% pure in nickel and sulfur, with the sulfur being present to a concentration of
from about 0.01% to about 5%, by weight.
81. The method of claim 77 wherein the electrolytic deposition forms silver over the
wiring layer; the electrolytic deposition occurs in a bath, and the bath is initially charged
with particulates that are at least 99.995% pure in silver.

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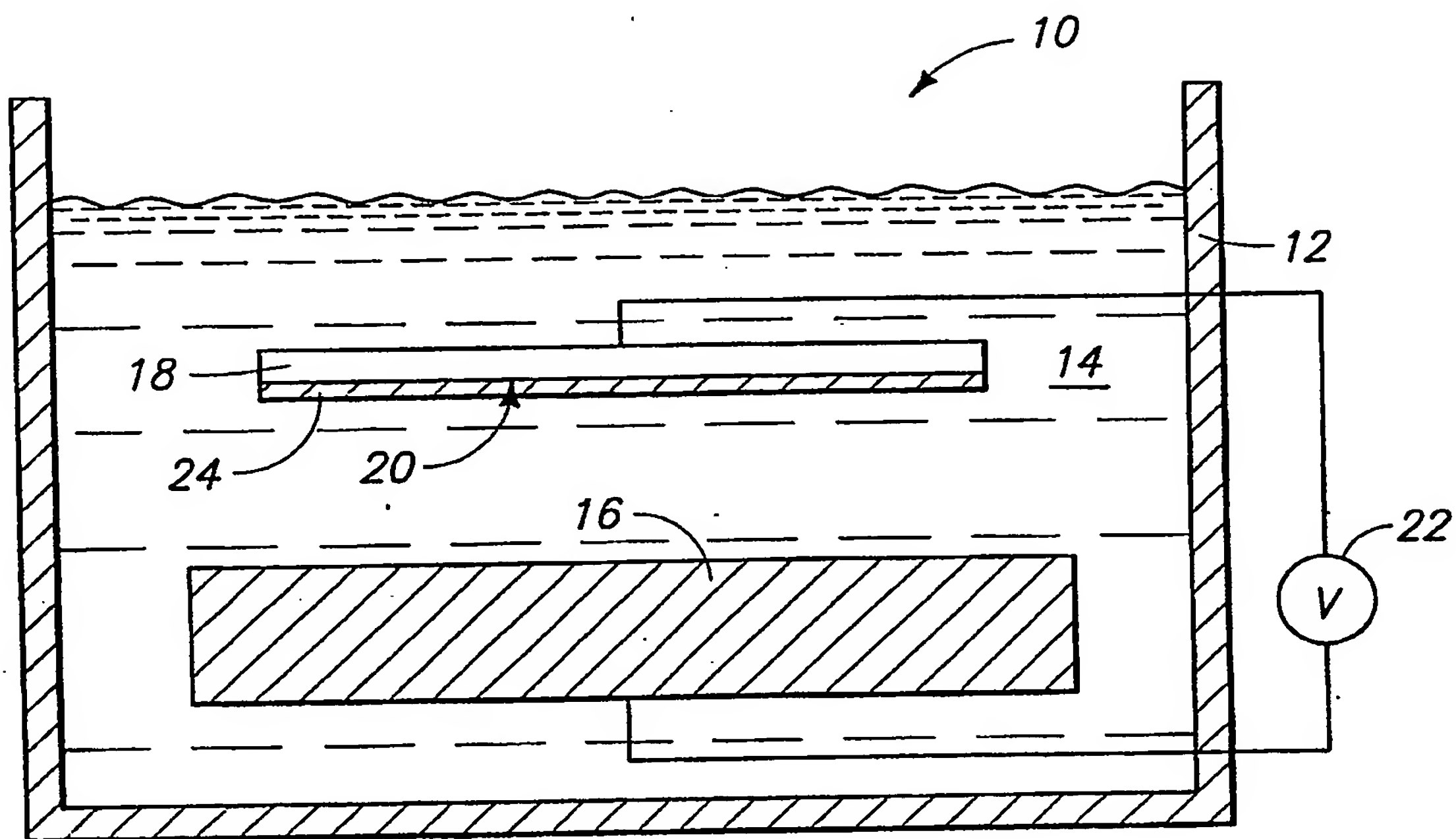


Fig. 1

PRIOR ART

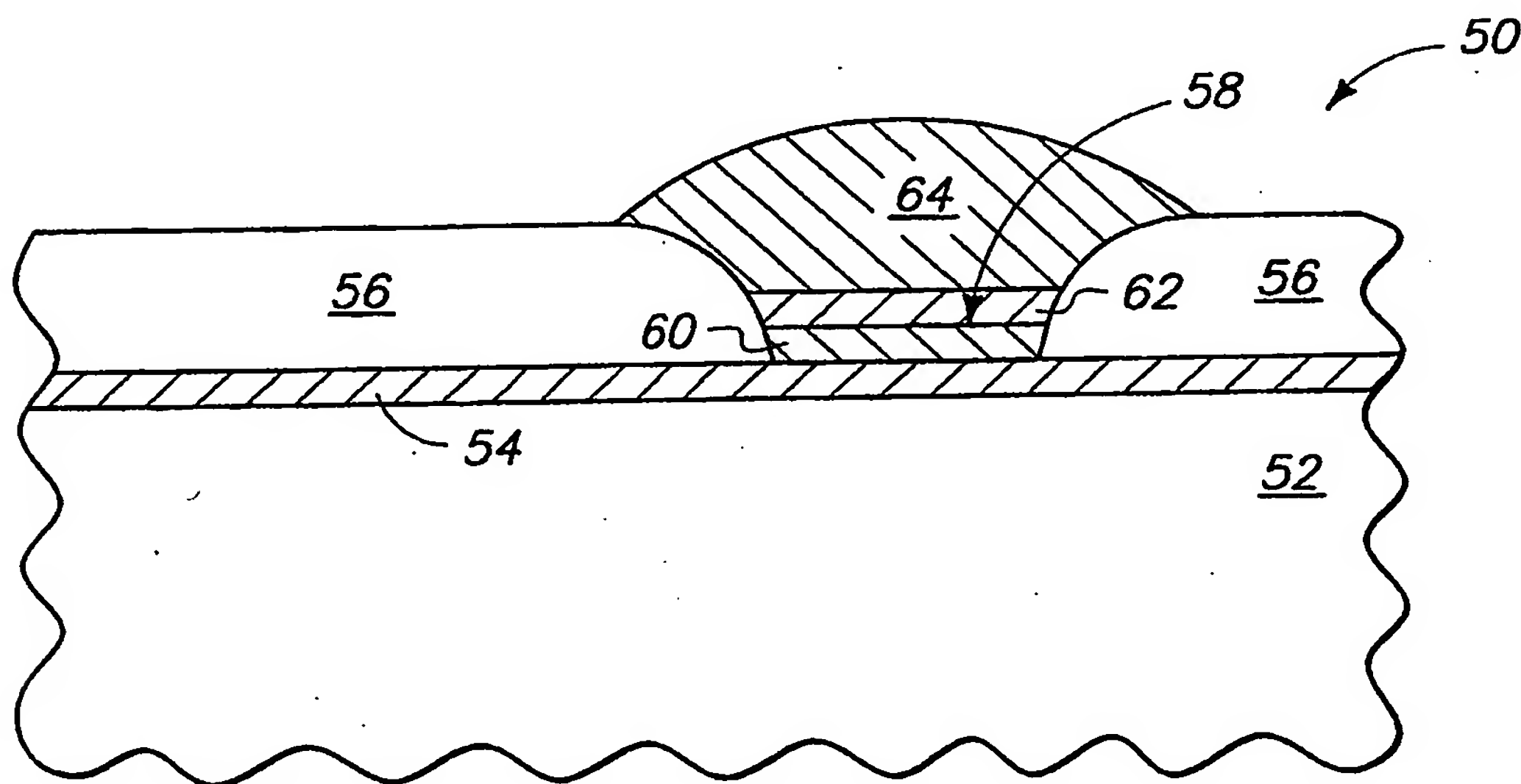
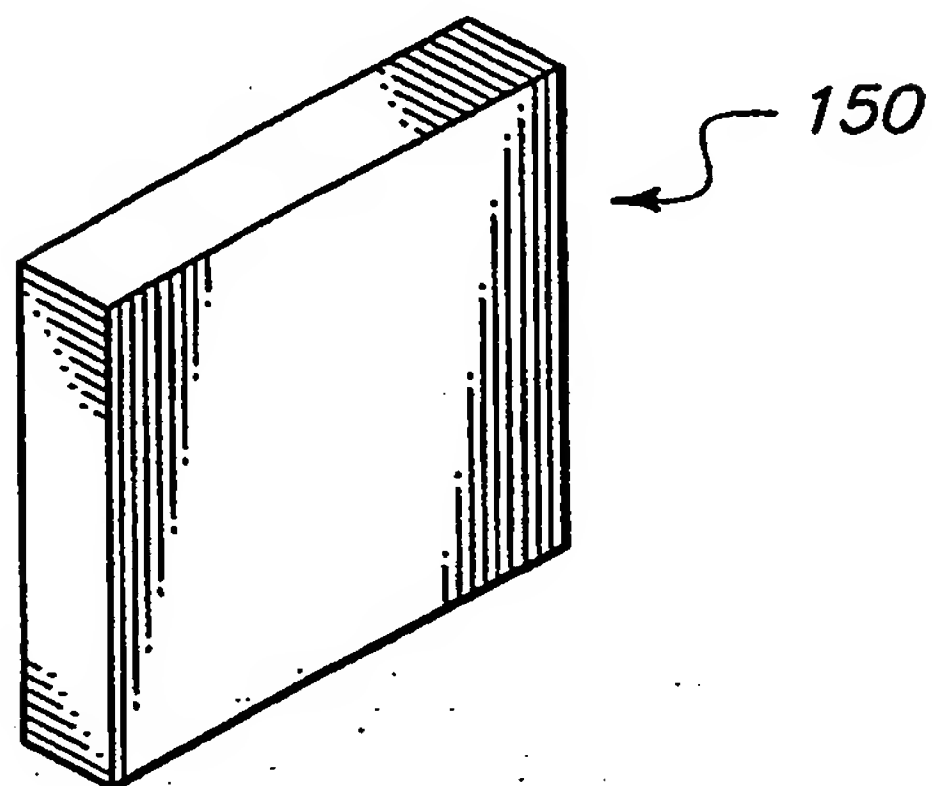
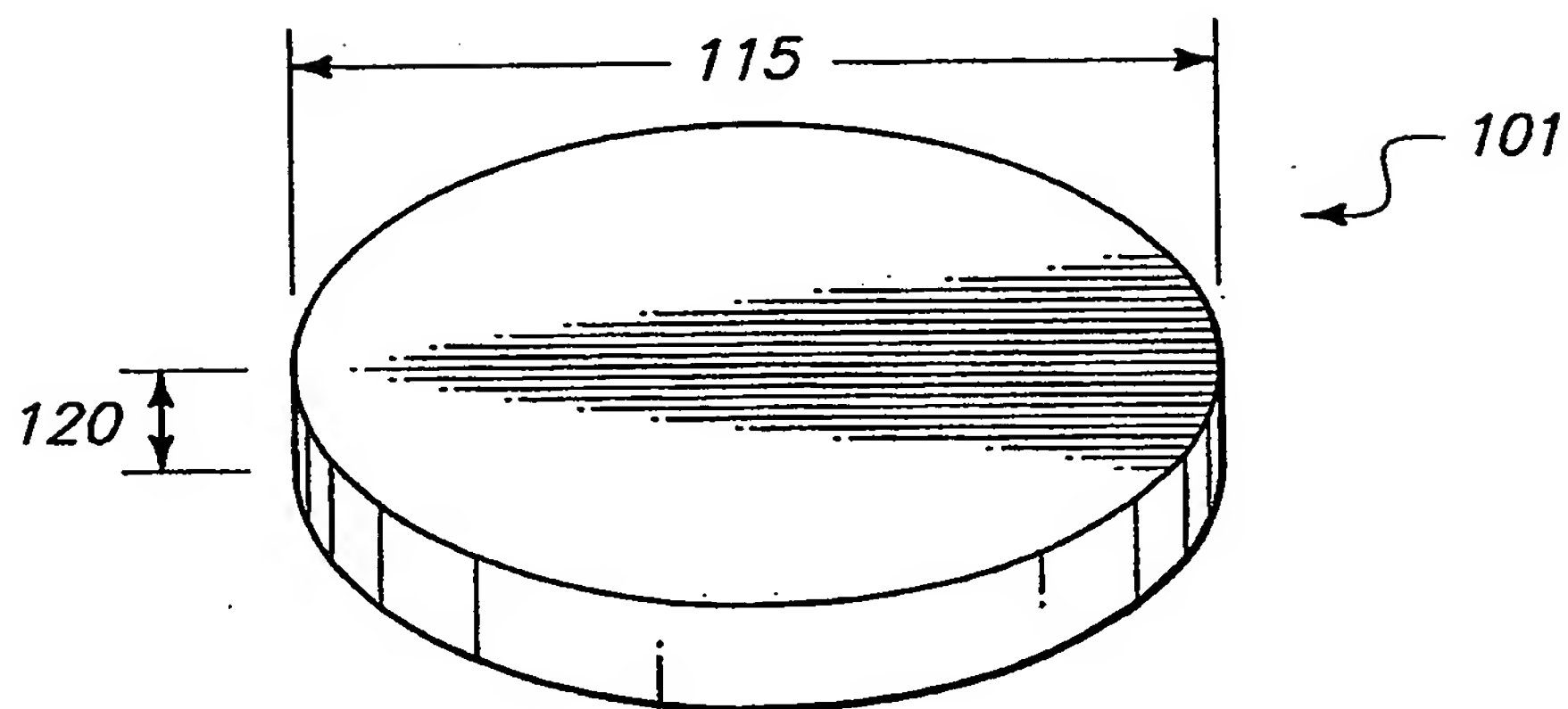
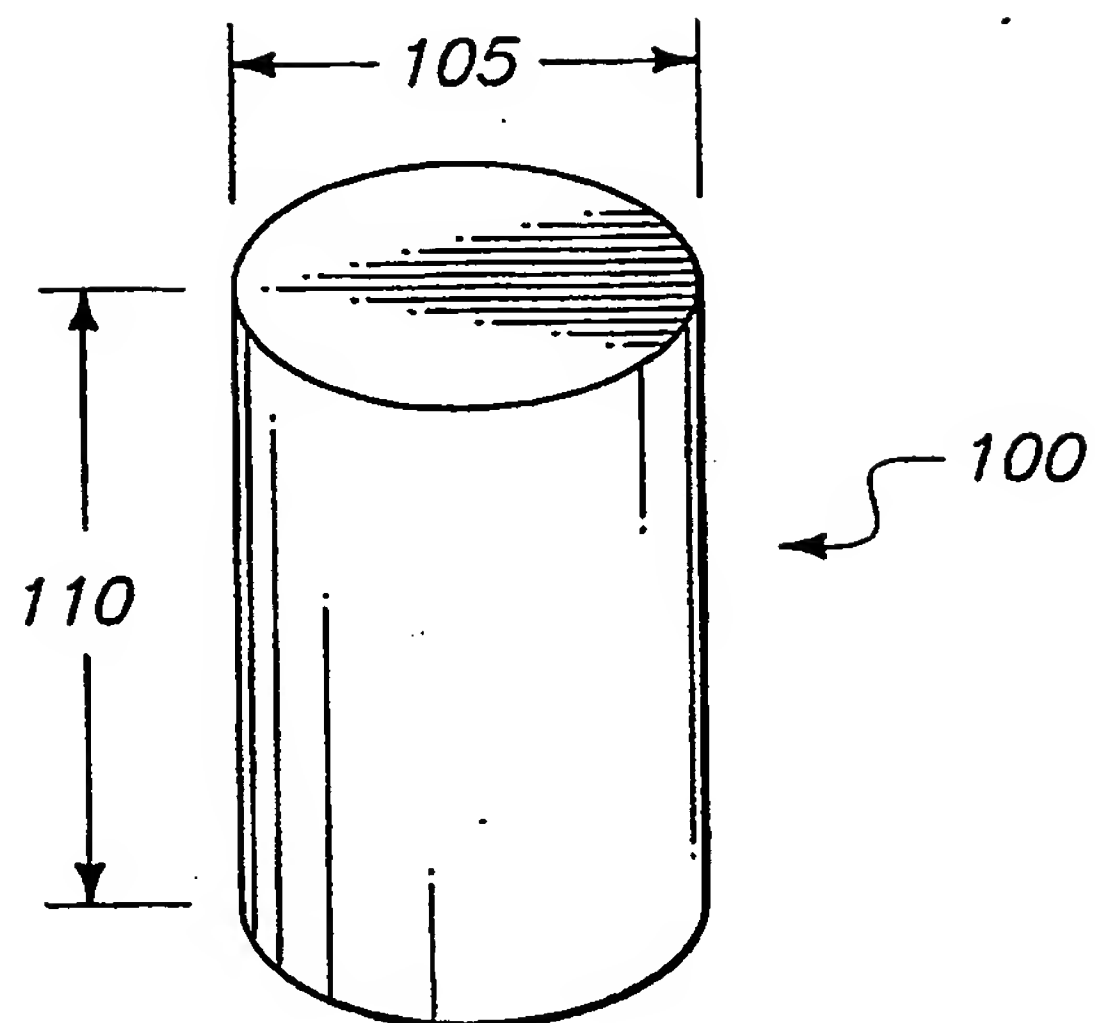


Fig. 2

PRIOR ART

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/44055

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25D7/12 C25D17/10 C25D1/04 C25D5/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C25D H05K C23C C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 5 780 755 A (DUNLOP JOHN ALDEN ET AL) 14 July 1998 (1998-07-14) cited in the application abstract column 4, line 12-23 -----	14-16

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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International Application No

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